PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-263049
(43)Date of publication of application : 26.09.2000

(51)Int.Cl. C02F 1/461
B01J 35/02
C02F 1/32
C02F 1/72
C02F 3/12

(21)Application number : 11-113996
(22)Date of filing : 18.03.1999

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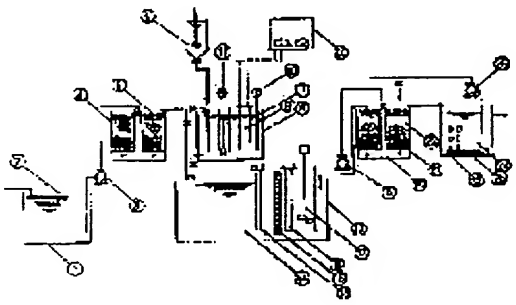
(54) METHOD AND APPARATUS FOR CLEANING BARN EFFLUENT

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method for cleaning barn effluent whereby a large amount of effluent can be treated; humic substances can be oxidatively decomposed economically; and the concentration of trihalometanes as a by-product is kept low enough to meet the effluent standard by adding a chloride and causing electricity to flow through while the pH is being adjusted to a specified value with an alkali agent when decomposing organic substances contained in an effluent formed by the activated sludge treatment of a barn sewage.



SOLUTION: A barn effluent 2 after an activated sludge treatment is transferred to a filtration vessel 4 to be adsorbed by a filtering material 5 and then is put into an electrolysis vessel 6 and a reaction vessel 13. An aqueous halogen compound solution, e.g. an aqueous common salt solution, from a chemical liquid vessel 9, is injected into the effluent 2 to be treated; some alkali agent is added to an aqueous solution adjusted so that the concentration of common salt is kept higher than 3% to prevent an electrode from being damaged, thus adjusting the pH to 6-7; and a rectifier 12 is switched on. After 30 min of electrolysis, an electrolytic solution 8 is injected into 10-50 times as much effluent 2, which is transferred from the filtration vessel 4 and stored in a reaction vessel 13, and is stirred with a stirrer 17 to be homogeneously mixed. Sodium hypochlorite synthesized in the electrolysis vessel 6 emits nascent oxygen as an oxidizing agent to oxidatively decolor huminic substances, a coloring component.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than

the examiner's decision of rejection or application converted registration]

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[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

(19)日本国特許庁（ＪＰ）　(12)公開特許公報（Ａ）　(11)特許出願公開番号
特開2000－263049
（P2000－263049A）
(43)公開日　平成12年９月26日(2000.9.26)

(51)Int.Cl.⁷		識別記号	FI		テーマコード（参考）
C02F	1/461		C02F	1/46	101C 4D028
B01J	35/02		B01J	35/02	J 4D037
C02F	1/32		C02F	1/32	4D050
	1/72	101		1/72	101 4D061
	3/12			3/12	F 4G069

審査請求　未請求　請求項の数３　書面　（全 5 頁）

(21)出願番号　特願平11－113996

(22)出願日　平成11年３月18日(1999.3.18)

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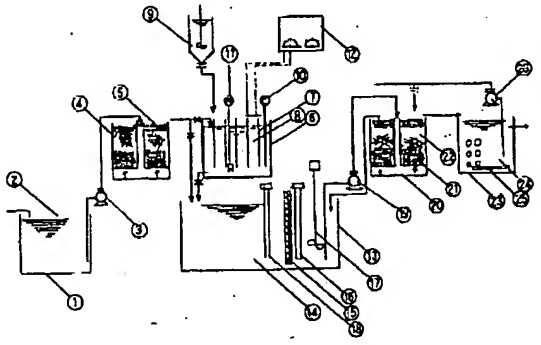
(54)【発明の名称】　畜舎排水の浄化処理法及びその装置

(57)【要約】
【課題】畜舎排水の難生物分解性有機物を効果的に酸化分解して脱色すると同時に副生するトリハロメタンも分解除去する技術とその装置を開発すること。
【解決手段】畜舎排水に塩化物を添加して電解処理するにあたり、酸化力が大きい成分の濃度を高めるため、電解液のｐＨ範囲を限定し、電極にダメージを与えない塩化物の添加量で電解し、しかる後大量の未電解排水を混合して、酸化反応させる際に副生するトリハロメタンを固型光触媒上で紫外線照射のもとに分解する。



【特許請求の範囲】
【請求項１】畜舎から排水される汚水を活性汚泥処理した排水中の有機物を電解処理するにあたり、塩化物を添加後アルカリ剤によってｐＨ６～８に調整しつつ通電することを特徴とする排水の処理方法。
【請求項２】畜舎から排出される汚水を活性汚泥処理した排水中の有機物を酸化処理するにあたり、電極にダメージを与えない３％以上の量の塩化物を添加、電解処理した液に対し１０～５０倍量の未電解排水液を混合撹拌することを特徴とする排水の処理方法。
【請求項３】畜舎から排出される汚水を活性汚泥処理した排水中の有機物を電解酸化処理後に副生するトリハロメタンを分解除去するにあたり、酸化反応中、光触媒を網篭に入れて反応液中に浸し、その近くから紫外線を照射することを特徴とする排水の処理方法。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、排水中に含まれる有機物を次亜塩素酸ソーダ存在下紫外線を照射することにより酸化分解し、排水中の着色成分を除去すると同時に本プロセスで副生するトリハロメタンを紫外線照射された光触媒固体表面上で分解除去するプロセスに関するものである。
【０００２】
【従来の技術】牛、豚等の畜舎から排出される汚水は、一般的には活性汚泥による浄化処理後、放流されている。ところが近年このような処理後の放流に対して、環境汚染と生活安全の面から大きく問題視されている。
【０００３】畜産汚水の浄化処理施設からの排水は濃度の差こそあれ薄黄色ないし茶褐色を呈している。この着色の主要因は水中に含まれるフミン質（有機物の最終化合物）であり、このフミン質を含有した処理水が河川に放流された場合、自然環境、自然生態系を破壊するばかりでなく、人の生活形態にも影響を与える。つまり河川の下流に浄水場がある場合、消毒のために塩素処理されるわけであるが、フミン質と塩素が反応して有害物質であるトリハロメタンが生成する。当然浄化処理施設からの排水そのものにもトリハロメタンが多く含有することは許されない。
【０００４】従って今後、畜舎汚水の浄化処理施設からの処理水には（１）フミン質の含有量がきわめて少なく、排水が着色していないことと、（２）トリハロメタンもきわめてわずかしか含有されていないことが社会的に要求される。
【０００５】（１）の排水の脱色に関しては、これまで多くの方法が試みられてきた。例えば凝集沈澱法、活性炭吸着法、分離膜法、オゾン処理法、過酸化水素法、紫外線酸化法、塩素系酸化剤法などが知られている。
【０００６】まず凝集沈澱法は、硫酸アルミニウム、ポリ塩化アルミニウム、硫酸第一鉄や硫酸第二鉄などの凝集剤を排水と混合、反応させて着色成分を凝集沈澱させ、上澄み液を放流させる方法であるが、凝集沈澱物を処理する工程が増える欠点がある。
【０００７】活性炭吸着法は活性炭に排水を通して着色成分を吸着させる方法であるが、活性炭の吸着能力が限られるという寿命の短さが致命的である。従って交換を頻繁に行い使用済の活性炭を廃棄する問題もあり、経済性も含め実用的でない。
【０００８】分離膜法は着色成分としての物質を沪過除去する技術であるが、着色成分の濃度が高く沪過量も多い畜舎排水処理では目詰まりしやすく、凝集液の再処理も必要となり実用性の面で好ましくない。
【０００９】オゾン処理法はオゾナイザーにより高濃度のオゾンを発生させ、排水中に曝気させオゾンの酸化力で脱色する方法であるが、畜舎排水のような高色度の処理には極めて高濃度のオゾンを必要とするため、経済的でなく、また高濃度オゾンは新たなオゾン処理が必要となる欠点がある。
【００１０】過酸化水素法は過酸化水素水の分解で生成するヒドロキシラジカルで着色成分を酸化分解させる方法であるが、処理速度はかなり遅い。そこで紫外線を併用したり、他の薬剤や技術との組合せも検討されているが、大量の畜舎排水には能力的に劣る。
【００１１】紫外線酸化法は波長域が２５４ｎｍの短波長の紫外線を排水中の有機物質に照射して分解することを基本としているが、難分解性有機物もあり、かなり困難である。そこで、他の方法と併用することや、オゾンを生成する１８５ｎｍの短波長も放射するランプを使用するなど検討されている。しかしこの方法も短時間に大量の排水処理するには困難である。
【００１２】塩素系酸化剤法は次亜塩素酸ソーダなどで化学的に有機物を酸化する方法として知られ、ＣＯＤやＢＯＤの原因となる有機物や色度成分を酸化するのに有効であることは広く知られている。しかし、ランニングコストが大きいと考えられ処理水量が多い場合には一般に使われていない。また、処理水に有機物との反応による有害なトリハロメタンの生成が懸念され好ましいプロセスと考えられていない。
【００１３】
【発明が解決しようとする課題】上記の諸方法は、それぞれ畜舎排水の脱色効果はあるが、短時間に大量の処理能力に欠けるとか、経済性に問題があるとか、二次処理を必要とするとか、有害物質を副生するとか一長一短を有している。本発明は上記の諸方法の中で短時間に大量の脱色効果を有する方法を最優先に考慮して、塩素系酸化剤法が最も好ましい方法として取上げ、ランニングコストを技術的な工程面から低減、塩素系酸化剤による有害なトリハロメタンが出来ずらい条件、また出来たものを分解することを課題としている。
【００１４】本発明は、ランニングコストとしての経済

性をどのようなプロセスにすれば妥当なものに出来るか、また、当然生成するトリハロメタン等の有害なハロゲン化物を分解して少なくすることを目的に、排水の処理方法と装置を提供することを目的としている。

【0015】

【課題を解決するための手段】本発明は上記目的を達成するため鋭意検討した結果（1）畜舎排水を処理する方法において排水の一部にハロゲン化物を添加し、電気分解した後に、過剰の畜舎排水を有する反応槽に注入し、廃液中に固定された固型光触媒に紫外線を照射しつつ常温で撹拌して脱色を行うと同時に、副生したトリハロメタン等の塩素化合物を光分解することを特徴とする。

【0016】（2）畜舎排水を処理する装置において予め沪過された排水の一部にハロゲン化合物を添加溶解させ、陽極には白金メッキチタン電極、陰極にステンレス電極を用いた電解槽にて通電処理する。これをアルカリ剤でｐＨを調整し、過剰の畜舎排水を有する反応槽に注入して常温下で撹拌し過剰の畜舎排水を酸化脱色させる。この際液内のフミン質と反応して生成すると思われるトリハロメタン等は反応槽の液内の網篭内に固定された光触媒に接触して、触媒表面に照射される低圧水銀ランプの光により分解される。反応終了後は沪過後残留塩素を含んだ沪過水は放流に先だち曝気して低残留塩素含有水とされる。

【0017】

【発明の実施の形態】以下、本発明の一実施形態を添付の図面に基づいて具体的に説明する。図１において、１は活性汚泥処理後の排水貯蔵槽であり、活性汚泥処理後の畜舎排水２が収容されている。活性汚泥処理後の畜舎排水２を排水供給ポンプ３により沪過槽４に移動し吸着性能を有するセラミックボールである沪過材５によって吸着後、電解槽６と反応槽１３に入れる。

【0018】電解槽６の電極板７の陽極は白金メッキチタン網状板を使用し、陰板にはＳＵＳ３０４を用いる。薬液槽９からハロゲン化合物水溶液例えば食塩水溶液が処理液に注入され電極にダメージを与えないように食塩濃度が３％以下にならないように調整した水溶液にアルカリ剤を若干加えてｐＨ６～８に調整して整流器１２の電源を入れる。電解温度は５０℃以下に保つことが好ましく、必要に応じて電解槽６内に冷却コイルを設けて冷却する。ｐＨは６～８に保つことが好ましいがこれはCl_2を少なくして、酸化能力のある次亜塩素酸と次亜塩素酸イオンの分布が最も大きく占める範囲だからである。（日根文男著・電気化学反応操作と電解槽工学、化学同人）電解時の電圧はＤＣ１２Ｖ前後、電流密度は１０Ａ／dm^2程度、極間距離は、５０ｍｍである。

【0019】電解３０分後電解液８は１０～５０倍量の処理液２を沪過槽４より反応槽１３に移動して貯えられた中に注入される。室温で撹拌機１７によって撹拌し、均一に混合する。電解槽６で合成された次亜塩素酸ソーダ（ＮａＣｌＯ）は発生期の酸素（Ｏ）を酸化剤として放出し、着色成分であるフミン質を酸化し脱色する。

【0020】しかし電解液８にはCl_2やClO^-が存在するため、これらが活性汚泥処理後の畜舎排水２に含まれるフミン質と反応し、クロロホルム等の有害な所謂トリハロメタンを生成する。従ってこのトリハロメタンを分解して除去する必要がある。

【0021】有機ハロゲン分解のために紫外線照射のもとに二酸化チタンを粉末で添加することが考えられたが、この場合は水溶液が白濁して光が透過しずらくその効果は認められなかった。（特開平５－２６９３７８）。

【0022】しかし二酸化チタン等１５を固体状にして液中に固定し、紫外線ランプ１６を極近くにセットすれば光触媒である二酸化チタン表面に付着したトリハロメタンを光分解することができる。波長は３８５ｍｍが好ましいが２５４ｍｍでも効果はある。

【0023】色度３００～４００であった反応液１４が色度１～５０になった時点で反応液汲取りポンプ１９により沪過槽２０に移され、沪過材２１で浮遊物は除去されてオーバーフローして放流監視槽２３に移動する。

【0024】放流監視槽２３では散気管２５からエアが曝気されており、残留塩素があればエアレーションにより除去される。

【0025】処理液２４は放流監視槽２３よりオーバーフローして逐次放流される。

【0026】

【実施例】本発明を実施例により更に詳細に説明する。着色排水を酸化処理するために塩素系酸化剤単独使用の場合として電解槽に活性汚泥処理液６０リットルを入れこれに食塩１．８ｋｇ、苛性ソーダ２．５ｇを投入し撹拌してｐＨ７．２の均一相にした。液温１８℃で９．７～１１．５Ｖ、１９０Ａで３０分間通電した。電流密度は９．０５Ａ／dm^2で極間距離は５０ｍｍであった。尚、電極は陽極は白金メッキチタン網状板で陰極はステンレス板を用いた。通電して得られた液は無色透明である。この液の一部を汲み取り、１０倍量の色度３５０の着色排水でうすめて種々の条件で室温下３０分間撹拌反応させた結果を表１に示す。

【0027】

【表１】

実験	紫外線 245nm	撹拌 r.p.m	光触媒	色度	トリハロメタン (mg/l)
1	−	120	−	40	0.925
2	○	120	−	4	0.915
3	○	120	ZnO	2	0.745
4	○	120	TiO_2	1	0.772

【0028】表1から明らかなように、撹拌と紫外線照射だけではトリハロメタンの分解は認められないが光触媒を使用することによって分解が確認される。

【0029】なお、実験1では反応が遅いため色度が大きいが時間がたつにつれて色度は小さくなって行く傾向にある。また、実験3のCODは8．6で出発原液の10分の1に減少していた。

【0030】

【発明の効果】本発明により、従来の塩素系酸化剤法としての次亜塩素酸ソーダ法よりも、電極を傷めずに酸化に有効な次亜塩素酸成分を生成出来、しかも多量の排液でうすめて反応させるため、処理量が多く経済的にフミン質の酸化分解が行える。更に、副生する有害なトリハロメタンもそれ程多量にはできず、もし生成しても固型の光触媒の使用により光分解されるためトリハロメタンの排出規制に十分適合出来る範囲以下である。

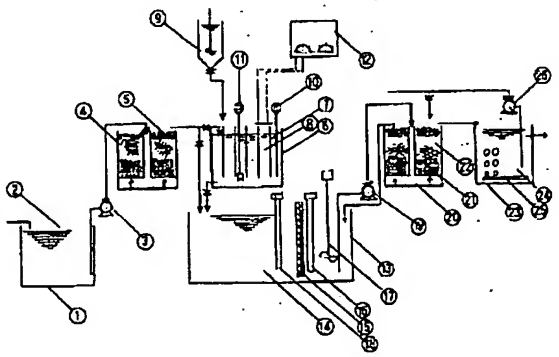
【図面の簡単な説明】

【図1】に本発明を実施する処理装置の1例を概要図でもって示す。

【符号の説明】

①・・・・活性汚泥処理後の排水貯蔵槽
②・・・・活性汚泥処理後の畜舎排水
③・・・・排水供給ポンプ
④・・・・沪過槽
⑤・・・・沪過材
⑥・・・・電解槽
⑦・・・・電極板
⑧・・・・電解液
⑨・・・・薬液槽
▲10▼・・・・温度計
▲11▼・・・・pH計
▲12▼・・・・整流器
▲13▼・・・・反応槽
▲14▼・・・・反応液
▲15▼・・・・光触媒
▲16▼・・・・紫外線ランプ
▲17▼・・・・撹拌機
▲18▼・・・・色度計
▲19▼・・・・反応液汲み取りポンプ
▲20▼・・・・沪過槽
▲21▼・・・・沪過材
▲22▼・・・・沪液
▲23▼・・・・放流監視槽
▲24▼・・・・処理液
▲25▼・・・・散気管
▲26▼・・・・処理液回収ポンプ

【図1】



フロントページの続き

Fターム(参考) 4D028 AB00
4D037 AA13 AB14 BA18 CA04 CA07
CA11
4D050 AA14 AB03 AB11 BB06 BC04
BC09 CA10 CA17
4D061 DA08 DB19 EA02 EA03 EB01
EB12 EB17 EB19 EB30 EB31
ED13 FA07 FA11 FA15 FA16
4G069 AA01 AA08 AA15 BA04A
BA48A CA05 CA07 CA10
CA15 DA06

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CLAIMS

[Claim(s)]
[Claim 1] The art of the wastewater characterized by energizing in carrying out electrolysis processing of the organic substance under wastewater which carried out activated sludge treatment of the sanitary sewage drained from a barn, the alkali chemicals after addition adjusting a chloride to pH 6-8.
[Claim 2] The art of the wastewater characterized by in oxidizing the organic substance under wastewater which carried out activated sludge treatment of the sanitary sewage discharged from a barn adding the chloride of 3% or more of amount which does not give a damage to an electrode, and carrying out mixed stirring of the non-electrolyzed wastewater liquid of an amount ten to 50 times to the liquid which carried out electrolysis processing.
[Claim 3] The art of the wastewater characterized by in carrying out decomposition clearance of the trihalomethane which carries out the byproduction of the organic substance under wastewater which carried out activated sludge treatment of the sanitary sewage discharged from a barn after electrolytic oxidation processing putting a photocatalyst into a net basket, dipping into reaction mixture during oxidation reaction, and irradiating ultraviolet rays near it.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention carries out oxidative degradation of the organic substance contained during wastewater by irradiating the bottom ultraviolet rays of sodium hypochlorite existence, and it relates to the process which carries out decomposition clearance of the trihalomethane which carries out a byproduction in this process on the photocatalyst solid-state front face by which UV irradiation was carried out at the same time it removes the coloring component under wastewater.
[0002]
[Description of the Prior Art] Generally the sanitary sewage discharged from barns, such as a cow and a pig, is discharged after the clarification processing by active sludge. However, it is greatly regarded as questionable from the field of environmental pollution and life insurance to the discharge after such [in recent years] processing.
[0003] the wastewater from the clarification treatment facility of the zootechnics sanitary sewage -- the difference of concentration -- that -- thin yellow thru/or blackish brown are presented. The key factor of this coloring is humus (the last compound of the organic substance) contained underwater, and when the treated water containing this humus is discharged to a river, it it not only destroys natural environment and natural ecosystem, but affects people's life-form voice. That is, although it is chlorinated for disinfection when purification plant is located on the lower stream of a river of a river, humus and chlorine react and the trihalomethane which is harmful matter generates. Trihalomethane is not allowed to contain mostly from the clarification treatment facility to the wastewater itself naturally.
[0004] Therefore, there are very few contents of (1) humus from the clarification treatment facility of the barn sanitary sewage to treated water, and it will be required socially from now on that wastewater is not coloring and that deer content of the (2) trihalomethane should not be carried out very only.
[0005] The approach of the former many has been tried about decolorization of wastewater of (1). For example, coagulating sedimentation, an activated-charcoal-absorption method, a demarcation membrane method, the ozone approach, the hydrogen-peroxide method, the ultraviolet-rays oxidation style, the chlorine-based oxidizer method, etc. are learned.
[0006] First, coagulating sedimentation is mixed [wastewater and], makes flocculants, such as an aluminum sulfate, a polyaluminum chloride, a ferrous sulfate, and ferric sulfate, react, and carries out coagulation sedimentation of the coloring component, and although it is the approach of making a supernatant discharging, there is a fault whose process which processes a coagulation sedimentation object increases.
[0007] Although an activated-charcoal-absorption method is an approach of making a coloring component sticking to activated carbon through wastewater, the shortness of the life that the adsorption capacity force of activated carbon is restricted is fatal. Therefore, there is also a problem which discards deed used activated carbon frequently about exchange, and it is not practical including profitability, either.
[0008] Although a demarcation membrane method is a technique which carries out filtration

clearance of the matter as a coloring component, in the barn waste water treatment also with many amounts of filtration where the concentration of a coloring component is high, it is easy to carry out blinding, reprocessing of condensation liquid is also needed, and it is not desirable in respect of practicability.

[0009] Although it is the approach of an ozone approach making generate high-concentration ozone with an ozonizer, making it carry out aeration during wastewater, and decolorizing by the oxidizing power of ozone, since very high-concentration ozone is needed for processing of a high chromaticity like barn wastewater, high concentration ozone has economically the fault for which new ozonization is needed.

[0010] Processing speed is quite slow although a hydrogen-peroxide method is the approach of carrying out oxidative degradation of the coloring component by the hydroxy radical generated by disassembly of hydrogen peroxide solution. Then, although ultraviolet rays are used together or other drugs and combination with a technique are also examined, it is inferior to barn wastewater of a large quantity in capacity.

[0011] Although the ultraviolet-rays oxidation style is based on a wavelength region irradiating and decomposing into an organic substance while draining the ultraviolet rays of the short wavelength which is 254nm, it also has the difficulty resolvability organic substance and is quite difficult. Then, it inquires using the lamp which also emits using together with other approaches, and the short wavelength of 185nm which generates ozone etc. however, this approach -- a short time -- a large quantity -- it is difficult for carrying out waste water treatment.

[0012] A chlorine-based oxidizer method is learned as an approach of oxidizing the organic substance chemically by sodium hypochlorite etc., and it is known widely that it is effective in oxidizing the organic substance leading to COD or BOD and a chromaticity component. However, it is thought that a running cost is large, and when there is much quantity of water to be treated, generally it is not used. Moreover, treated water is anxious about generation of the harmful trihalomethane by the reaction with the organic substance, and it is not considered a desirable process.

[0013]

[Problem(s) to be Solved by the Invention] Although there is the decolorization effectiveness of barn wastewater, respectively, many above-mentioned approaches lack in the throughput of a large quantity for a short time, or a problem is in profitability, they need secondary treatment, carry out the byproduction of the harmful matter, or have merits and demerits. It is making for a chlorine-based oxidizer method to take up as most desirable approach to top priority in consideration of the approach of having the decolorization effectiveness of a large quantity in many above-mentioned approaches for a short time, and for the harmful trihalomethane by reduction and the chlorine-based oxidizer to be unable to do a running cost from a technical process side, but for this invention to decompose **** conditions and the made thing into the technical problem.

[0014] This invention aims at offering the art and equipment of wastewater for the purpose of disassembling harmful halogenides, such as trihalomethane which is made to an appropriate thing or is naturally generated, and lessening, if profitability as a running cost is made into what kind of process.

[0015]

[Means for Solving the Problem] It is characterized by to photodissociate chlorine compounds, such as trihalomethane which carried out the byproduction, at the same time it pours into the reaction vessel which has superfluous barn wastewater, and it stirs it in ordinary temperature, irradiating ultraviolet rays at the solid photocatalyst fixed in waste fluid and it decolorizes, after this invention adds and electrolyzes a halogenide into some wastewater in the approach of processing (1) barn wastewater as a result of inquiring wholeheartedly, in order to attain the above-mentioned object.

[0016] (2) Make some wastewater beforehand filtered in the equipment which processes barn wastewater carry out the addition dissolution of the halogenated compound, and carry out energization processing in an anode plate with the cell which used the stainless steel electrode for a platinum plating titanium electrode and cathode. pH is adjusted for this by alkali chemicals,

and it pours into the reaction vessel which has superfluous barn wastewater, and stirs under ordinary temperature, and oxidation decolorization of the superfluous barn wastewater is carried out. Under the present circumstances, the trihalomethane considered to react with the humus in liquid and to generate contacts the photocatalyst fixed in the net basket in the liquid of a reaction vessel, and is decomposed by the light of the low-pressure mercury lamp irradiated by the catalyst front face. Carry out aeration of the filtered water with which after reaction termination contained the residual chlorine after filtration in advance of discharge, and let it be low residual chlorine content water.

[0017]

[Embodiment of the Invention] Hereafter, based on the drawing of attachment of 1 operation gestalt of this invention, it explains concretely. In drawing 1 , 1 is a wastewater storage tank after activated sludge treatment, and the barn wastewater 2 after activated sludge treatment is held. It puts into a cell 6 and a reaction vessel 13 after adsorption with the filter media 5 which are the ceramic balls which move the barn wastewater 2 after activated sludge treatment to a lauter tub 4 by the wastewater feed pump 3, and have the adsorption engine performance.

[0018] The anode plate of the electrode plate 7 of a cell 6 uses a platinum plating titanium reticular lamina, and uses SUS304 for ****. Alkali chemicals are added to the water solution adjusted so that a halogenated compound water solution, for example, a brine solution, might be poured into processing liquid from the drug solution tub 9, a damage might not be given to an electrode and salt concentration might not become 3% or less a little, it adjusts to pH 6-8, and a rectifier 12 is turned on. Electrolysis temperature is desirable, if needed, keeping at 50 degrees C or less prepares a cooling coil in a cell 6, and it cools it. It is because this lessens Cl2 and distribution of a hypochlorous acid and a hypochlorite with oxidation capacity is the range occupied most greatly, although keeping at 6-8 is desirable as for pH. (Fumio Hine work and electrochemical reaction actuation, cell engineering, Kagaku-Dojin) The electrical potential difference at the time of electrolysis is [about two 10 A/dm and the distance between electrodes of current density] 50mm before and after DC12V.

[0019] The after [30 minutes] electrolytic solution 8 of electrolysis is poured into the inside which moved the processing liquid 2 of an amount to the reaction vessel 13 from the lauter tub 4 ten to 50 times, and was stored. It stirs with an agitator 17 at a room temperature, and mixes to homogeneity. The sodium hypochlorite (NaClO) compounded with the cell 6 emits the oxygen (O) of a nascent state as an oxidizer, and oxidizes and decolorizes the humus which is a coloring component.

[0020] However, since Cl2 and ClO- exist in the electrolytic solution 8, these react with the humus contained in the barn wastewater 2 after activated sludge treatment, and generate the so-called harmful trihalomethane, such as chloroform. Therefore, it is necessary to decompose and remove this trihalomethane.

[0021] Although it was possible to add a titanium dioxide with powder on the basis of UV irradiation for organic halogen decomposition, the water solution became cloudy in this case, light penetrated, and the effectiveness of ******** was not accepted. (JP,5-269378,A) .

[0022] However, the trihalomethane adhering to the titanium-dioxide front face which will be a photocatalyst if 15 is made into the shape of a solid-state, it fixes in liquid and a titanium dioxide etc. sets an ultraviolet ray lamp 16 near the pole can be photodissociated. Although 385mm of wavelength is desirable, it is effective at least 254mm.

[0023] When the reaction mixture 14 which was chromaticities 300-400 becomes chromaticities 1-50, it is moved to a lauter tub 20 with the reaction mixture dipping-up pump 19, and suspended matter is removed at filter media 21, and it overflows, and moves to the discharge monitor tank 23.

[0024] In the discharge monitor tank 23, if aeration of the air is carried out from the powder trachea 25 and there is residual chlorine, it will be removed by aeration.

[0025] Processing liquid 24 is overflowed from the discharge monitor tank 23, and is discharged serially.

[0026]

[Example] An example explains this invention to a detail further. In order to oxidize coloring

wastewater, 60l. of activated-sludge-treatment liquid was put into the cell as a case of a chlorine-based oxidizer independent activity, 1.8kg of salt and 2.5g of caustic alkali of sodium were thrown in and stirred to this, and it was made the homogeneity phase of pH7.2. It energized for 30 minutes by 9.7-11.5V, and 190A at 18 degrees C of solution temperature. The distance between electrodes of current density was 50mm in 9.05 A/dm2. In addition, as for cathode, in the anode plate, the electrode used the stainless plate by the platinum plating titanium reticular lamina. The liquid energized and obtained is transparent and colorless. A part of this liquid is drawn up and the result of having thinned with coloring wastewater of the chromaticity 350 of an amount 10 times, and carrying out the stirring reaction for bottom 30 minutes of a room temperature on condition that versatility is shown in a table 1.

[0027]

[A table 1]

実　験	紫外線 245nm	撹　拌 r.p.m	光触媒	色　度	トリハロメタン (mg／l)
1	−	120	−	40	0.925
2	○	120	−	4	0.915
3	○	120	ZnO	2	0.745
4	○	120	TiO_2	1	0.772

[0028] Although decomposition of trihalomethane is not accepted, decomposition is checked by using a photocatalyst only by stirring and UV irradiation, so that clearly from a table 1.

[0029] In addition, in experiment 1, a chromaticity is in the inclination which becomes small and goes as time amount is formed, although a chromaticity is large, since the reaction is slow. Moreover, COD of experiment 3 was decreasing to 1/10 of a start undiluted solution by 8.6.

[0030]

[Effect of the Invention] By this invention, rather than the sodium hypochlorite method as a conventional chlorine-based oxidizer method, a hypochlorous-acid component effective in oxidation can be generated without damaging an electrode, and since it is moreover made to thin and react with a lot of effluents, a throughput can perform many oxidative degradation of humus economically. Furthermore, the harmful trihalomethane which carries out a byproduction is also below the range that can suit the effluent control of trihalomethane enough so so much since a photolysis is carried out by the activity of a solid photocatalyst even if it generates, a showy flaw and.

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TECHNICAL FIELD

[Field of the Invention] This invention carries out oxidative degradation of the organic substance contained during wastewater by irradiating the bottom ultraviolet rays of sodium hypochlorite existence, and it relates to the process which carries out decomposition clearance of the trihalomethane which carries out a byproduction in this process on the photocatalyst solid-state front face by which UV irradiation was carried out at the same time it removes the coloring component under wastewater.

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PRIOR ART

[Description of the Prior Art] Generally the sanitary sewage discharged from barns, such as a cow and a pig, is discharged after the clarification processing by active sludge. However, it is greatly regarded as questionable from the field of environmental pollution and life insurance to the discharge after such [in recent years] processing.
[0003] the wastewater from the clarification treatment facility of the zootechnics sanitary sewage -- the difference of concentration -- that -- thin yellow thru/or blackish brown are presented. The key factor of this coloring is humus (the last compound of the organic substance) contained underwater, and when the treated water containing this humus is discharged to a river, it it not only destroys natural environment and natural ecosystem, but affects people's life-form voice. That is, although it is chlorinated for disinfection when purification plant is located on the lower stream of a river of a river, humus and chlorine react and the trihalomethane which is harmful matter generates. Trihalomethane is not allowed to contain mostly from the clarification treatment facility to the wastewater itself naturally.
[0004] Therefore, there are very few contents of (1) humus from the clarification treatment facility of the barn sanitary sewage to treated water, and it will be required socially from now on that wastewater is not coloring and that deer content of the (2) trihalomethane should not be carried out very only.
[0005] The approach of the former many has been tried about decolorization of wastewater of (1). For example, coagulating sedimentation, an activated-charcoal-absorption method, a demarcation membrane method, the ozone approach, the hydrogen-peroxide method, the ultraviolet-rays oxidation style, the chlorine-based oxidizer method, etc. are learned.
[0006] First, coagulating sedimentation is mixed [wastewater and], makes flocculants, such as an aluminum sulfate, a polyaluminum chloride, a ferrous sulfate, and ferric sulfate, react, and carries out coagulation sedimentation of the coloring component, and although it is the approach of making a supernatant discharging, there is a fault whose process which processes a coagulation sedimentation object increases.
[0007] Although an activated-charcoal-absorption method is an approach of making a coloring component sticking to activated carbon through wastewater, the shortness of the life that the adsorption capacity force of activated carbon is restricted is fatal. Therefore, there is also a problem which discards deed used activated carbon frequently about exchange, and it is not practical including profitability, either.
[0008] Although a demarcation membrane method is a technique which carries out filtration clearance of the matter as a coloring component, in the barn waste water treatment also with many amounts of filtration where the concentration of a coloring component is high, it is easy to carry out blinding, reprocessing of condensation liquid is also needed, and it is not desirable in respect of practicability.
[0009] Although it is the approach of an ozone approach making generate high-concentration ozone with an ozonizer, making it carry out aeration during wastewater, and decolorizing by the oxidizing power of ozone, since very high-concentration ozone is needed for processing of a high chromaticity like barn wastewater, high concentration ozone has economically the fault for which new ozonization is needed.

[0010] Processing speed is quite slow although a hydrogen-peroxide method is the approach of carrying out oxidative degradation of the coloring component by the hydroxy radical generated by disassembly of hydrogen peroxide solution. Then, although ultraviolet rays are used together or other drugs and combination with a technique are also examined, it is inferior to barn wastewater of a large quantity in capacity.
[0011] Although the ultraviolet-rays oxidation style is based on a wavelength region irradiating and decomposing into an organic substance while draining the ultraviolet rays of the short wavelength which is 254nm, it also has the difficulty resolvability organic substance and is quite difficult. Then, it inquires using the lamp which also emits using together with other approaches, and the short wavelength of 185nm which generates ozone etc. however, this approach -- a short time -- a large quantity -- it is difficult for carrying out waste water treatment.
[0012] A chlorine-based oxidizer method is learned as an approach of oxidizing the organic substance chemically by sodium hypochlorite etc., and it is known widely that it is effective in oxidizing the organic substance leading to COD or BOD and a chromaticity component. However, it is thought that a running cost is large, and when there is much quantity of water to be treated, generally it is not used. Moreover, treated water is anxious about generation of the harmful trihalomethane by the reaction with the organic substance, and it is not considered a desirable process.

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EFFECT OF THE INVENTION

[Effect of the Invention] By this invention, rather than the sodium hypochlorite method as a conventional chlorine-based oxidizer method, a hypochlorous-acid component effective in oxidation can be generated without damaging an electrode, and since it is moreover made to thin and react with a lot of effluents, a throughput can perform many oxidative degradation of humus economically. Furthermore, the harmful trihalomethane which carries out a byproduction is also below the range that can suit the effluent control of trihalomethane enough so so much since a photolysis is carried out by the activity of a solid photocatalyst even if it generates, a showy flaw and.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Although there is the decolorization effectiveness of barn wastewater, respectively, many above-mentioned approaches lack in the throughput of a large quantity for a short time, or a problem is in profitability, they need secondary treatment, carry out the byproduction of the harmful matter, or have merits and demerits. It is making for a chlorine-based oxidizer method to take up as most desirable approach to top priority in consideration of the approach of having the decolorization effectiveness of a large quantity in many above-mentioned approaches for a short time, and for the harmful trihalomethane by reduction and the chlorine-based oxidizer to be unable to do a running cost from a technical process side, but for this invention to decompose **** conditions and the made thing into the technical problem.
[0014] This invention aims at offering the art and equipment of wastewater for the purpose of disassembling harmful halogenides, such as trihalomethane which is made to an appropriate thing or is naturally generated, and lessening, if profitability as a running cost is made into what kind of process.

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MEANS

[Means for Solving the Problem] It is characterized by to photodissociate chlorine compounds, such as trihalomethane which carried out the byproduction, at the same time it pours into the reaction vessel which has superfluous barn wastewater, and it stirs it in ordinary temperature, irradiating ultraviolet rays at the solid photocatalyst fixed in waste fluid and it decolorizes, after this invention adds and electrolyzes a halogenide into some wastewater in the approach of processing (1) barn wastewater as a result of inquiring wholeheartedly, in order to attain the above-mentioned object.
[0016] (2) Make some wastewater beforehand filtered in the equipment which processes barn wastewater carry out the addition dissolution of the halogenated compound, and carry out energization processing in an anode plate with the cell which used the stainless steel electrode for a platinum plating titanium electrode and cathode. pH is adjusted for this by alkali chemicals, and it pours into the reaction vessel which has superfluous barn wastewater, and stirs under ordinary temperature, and oxidation decolorization of the superfluous barn wastewater is carried out. Under the present circumstances, the trihalomethane considered to react with the humus in liquid and to generate contacts the photocatalyst fixed in the net basket in the liquid of a reaction vessel, and is decomposed by the light of the low-pressure mercury lamp irradiated by the catalyst front face. Carry out aeration of the filtered water with which after reaction termination contained the residual chlorine after filtration in advance of discharge, and let it be low residual chlorine content water.
[0017]
[Embodiment of the Invention] Hereafter, based on the drawing of attachment of 1 operation gestalt of this invention, it explains concretely. In drawing 1 , 1 is a wastewater storage tank after activated sludge treatment, and the barn wastewater 2 after activated sludge treatment is held. It puts into a cell 6 and a reaction vessel 13 after adsorption with the filter media 5 which are the ceramic balls which move the barn wastewater 2 after activated sludge treatment to a lauter tub 4 by the wastewater feed pump 3, and have the adsorption engine performance.
[0018] The anode plate of the electrode plate 7 of a cell 6 uses a platinum plating titanium reticular lamina, and uses SUS304 for ****. Alkali chemicals are added to the water solution adjusted so that a halogenated compound water solution, for example, a brine solution, might be poured into processing liquid from the drug solution tub 9, a damage might not be given to an electrode and salt concentration might not become 3% or less a little, it adjusts to pH 6-8, and a rectifier 12 is turned on. Electrolysis temperature is desirable, if needed, keeping at 50 degrees C or less prepares a cooling coil in a cell 6, and it cools it. It is because this lessens Cl2 and distribution of a hypochlorous acid and a hypochlorite with oxidation capacity is the range occupied most greatly, although keeping at 6-8 is desirable as for pH. (Fumio Hine work and electrochemical reaction actuation, cell engineering, Kagaku-Dojin) The electrical potential difference at the time of electrolysis is [about two 10 A/dm and the distance between electrodes of current density] 50mm before and after DC12V.
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homogeneity. The sodium hypochlorite (NaClO) compounded with the cell 6 emits the oxygen (O) of a nascent state as an oxidizer, and oxidizes and decolorizes the humus which is a coloring component.

[0020] However, since Cl2 and ClO- exist in the electrolytic solution 8, these react with the humus contained in the barn wastewater 2 after activated sludge treatment, and generate the so-called harmful trihalomethane, such as chloroform. Therefore, it is necessary to decompose and remove this trihalomethane.

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[0022] However, the trihalomethane adhering to the titanium-dioxide front face which will be a photocatalyst if 15 is made into the shape of a solid-state, it fixes in liquid and a titanium dioxide etc. sets an ultraviolet ray lamp 16 near the pole can be photodissociated. Although 385mm of wavelength is desirable, it is effective at least 254mm.

[0023] When the reaction mixture 14 which was chromaticities 300-400 becomes chromaticities 1-50, it is moved to a lauter tub 20 with the reaction mixture dipping-up pump 19, and suspended matter is removed at filter media 21, and it overflows, and moves to the discharge monitor tank 23.

[0024] In the discharge monitor tank 23, if aeration of the air is carried out from the powder trachea 25 and there is residual chlorine, it will be removed by aeration.

[0025] Processing liquid 24 is overflowed from the discharge monitor tank 23, and is discharged serially.

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EXAMPLE

[Example] An example explains this invention to a detail further. In order to oxidize coloring wastewater, 60l. of activated-sludge-treatment liquid was put into the cell as a case of a chlorine-based oxidizer independent activity, 1.8kg of salt and 2.5g of caustic alkali of sodium were thrown in and stirred to this, and it was made the homogeneity phase of pH7.2. It energized for 30 minutes by 9.7-11.5V, and 190A at 18 degrees C of solution temperature. The distance between electrodes of current density was 50mm in 9.05 A/dm2. In addition, as for cathode, in the anode plate, the electrode used the stainless plate by the platinum plating titanium reticular lamina. The liquid energized and obtained is transparent and colorless. A part of this liquid is drawn up and the result of having thinned with coloring wastewater of the chromaticity 350 of an amount 10 times, and carrying out the stirring reaction for bottom 30 minutes of a room temperature on condition that versatility is shown in a table 1.
[0027]
[A table 1]

実　験	紫外線 245nm	撹　拌 r.p.m	光触媒	色　度	トリハロメタン (mg/l)
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[0028] Although decomposition of trihalomethane is not accepted, decomposition is checked by using a photocatalyst only by stirring and UV irradiation, so that clearly from a table 1.
[0029] In addition, in experiment 1, a chromaticity is in the inclination which becomes small and goes as time amount is formed, although a chromaticity is large, since the reaction is slow. Moreover, COD of experiment 3 was decreasing to 1/10 of a start undiluted solution by 8.6.

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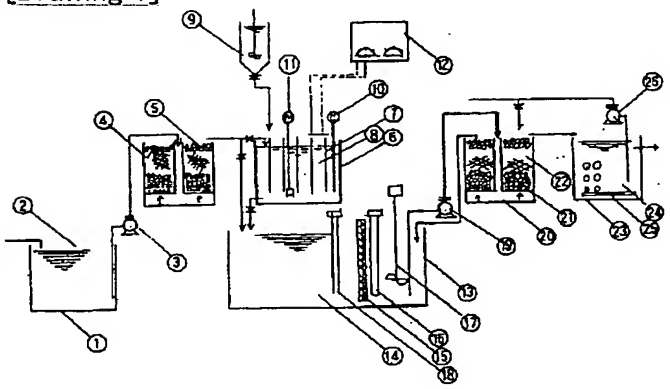
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is indicated that a schematic diagram is also about one example of a processor which is alike and carries out this invention.
[Description of Notations]
** .... Wastewater storage tank after activated sludge treatment
** .... Barn wastewater after activated sludge treatment
** .... Wastewater feed pump
** .... Lauter tub
** .... Filter media
** .... Cell
** .... Electrode plate
** .... Electrolytic solution
** .... Drug solution tub
**10 .... Thermometer
**11 .... PH meter
**12 .... Rectifier
**13 .... Reaction vessel
**14 .... Reaction mixture
**15 .... Photocatalyst
**16 .... Ultraviolet ray lamp
**17 .... Agitator
**18 .... Chromoscope
**19 .... Reaction mixture dipping-up pump
**20 .... Lauter tub
**21 .... Filter media
**22 .... Filtrate
**23 .... Discharge monitor tank
**24 .... Processing liquid
**25 .... Powder trachea
**26 .... Processing liquid recovery pump

[Translation done.]

DRAWINGS

[Drawing 1]



[Translation done.]